

The study of carbon-based lead foam as positive current collector of lead acid battery

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Abstract The carbon-based lead foam was produced by electrodeposition a uniform and dense lead coating on lightweight carbon foam in fluoborate system under appropriate conditions. The cyclic voltammetry showed that its electrochemical properties resembled the metallic pure lead. A lead acid battery equipped with the carbon-based lead foam as positive current collector undergone a charge–discharge test. The battery had a high discharge capacity and a good cycling stability, which indicated that the carbon-based lead foam could serve as positive current collector. The three-dimensional net structure of carbon-based lead foam provides larger surface area than traditional lead alloy grids, thus enhances the specific capacity of lead acid battery. The carbon-based lead foam might be a promising substitute for lead alloy grids.

Keywords Carbon foam · Electrodeposition · Lead acid battery · Positive current collector

1 Introduction

Lead acid batteries are applied widely in the standby power and other energy storage devices due to their high-current discharge performance, no memory effect, mature production techniques, safety and reliability. However, the traditional

lead acid battery exhibits relatively low specific capacity, short life cycle and bad rapid charge–discharge performance, which cannot meet today's demand on energy, transportation and power [1]. The internationally well-known American company of Caterpillar added an R & D department named Firefly Energy Inc. in 2003. The purpose was to develop lead acid batteries with more excellent performance.

As one of important means to improve the specific capacity of lead acid batteries, the use of lightweight materials to replace the lead acid batteries' heavy lead alloy collectors caught the attention of scholars worldwide. Aluminum, copper mesh, plastic, ceramic and other materials with lead coating were employed as the grids. The lead-covered glass woven fabric was also used as grids. Moreover, conductive inorganic compounds, such as carbon materials [2], SnO_2 [3], Ti, V, Mo, Nb oxides [4], oxides with perovskite structure [5] or other compounds [6] were also chosen to be grids.

Carbon foam, displaying its advantages of lightweight, three-dimensional net structures, large specific surface area, good corrosion resistance and high electrical conductivity, is a promising candidate, especially for the direct application as negative current collector [7, 8]. The preparation process of carbon foams includes foaming, carbonization and graphitization [9]. If carbon foam can be used in lead acid battery, it can reduce the use of lead, which not only reduces the weight of the battery, but also conducive to environmental protection. However, for the employment as positive current collector, carbon foam still faces some problems. Yong-Il Jang et al. [7] used graphite foams and non-graphitized foams as positive current collectors for lead acid batteries, respectively. The battery tests showed that because of the intercalation and deintercalation of bisulfate ions and sulfuric acid molecules between graphite layers in the positive voltage range,

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graphite foams could not be used as positive current collectors while the non-graphitized ones could. However, Ya Chen et al. [8] pointed out that due to the oxygen evolution, non-graphitized foams could not be used as positive current collectors either. So the physical and/or chemical modification was necessary to make carbon foams suitable to serve as positive current collectors. Elod Gyenge [10] investigated the reticulated vitreous carbon electroplated with a Pb–Sn (1 wt%) alloy as current collectors for lead acid batteries. The positive active material utilization efficiency of the battery equipped with these current collectors was up to 21 %. B. Hariprakash et al. [11] prepared lightweight grids from flexible graphite sheets which were coated with a lead layer followed by a corrosion-resistant polyaniline layer. But the cycle life of the lead acid cell with these lightweight grids was not satisfying.

Carbon foam was modified by electrodeposition of lead to prepare carbon-based lead foam for lead acid battery positive grid, and the pure lead was chosen to be cathodic grid. The SEM, cyclic voltammetry technique and the battery charge–discharge experiments were applied to study morphology, electrochemical properties and battery performance of the lightweight carbon-based lead foam grid in this paper.

2 Experimental

Carbon-based lead foam was prepared by electrodeposition. The substrate was carbon foam slab (25 mm × 5 mm × 40 mm) prepared by template method [12], whose specific surface area was 89 cm²·cm^{−3}. Before electrodeposition, these carbon foam substrates were dipped in acetone under ultrasonic for 10 min to remove oil. Then they were rinsed with pure water and dried at 50 °C for 1 h. The lead coatings were electroplated from complex system and fluoborate system, respectively. The composition of the different plating bath and technical conditions are shown in Table 1. All chemicals used in this work were of analytical grade. The pH of the complex system was adjusted to 5–6 with concentrated NH₃·2H₂O. The carbon-based lead foam was

repeatedly rinsed with pure water after electrodeposition and finally dried at room temperature.

Morphology of carbon-based lead foam deposited from different systems was examined under a JSM-6360 LV scanning electron microscope (SEM). The cyclic voltammetry was performed using a CHI660B electrochemical workstation at a scan rate of 5 Mv s^{−1} in a three-electrode cell. An Hg/Hg₂SO₄ electrode in saturated K₂SO₄ solution (MSE) was utilized as the reference electrode and a piece of platinum with an exposed area equal to 4 cm² was employed as the counter electrode. A H₂SO₄ solution (4.5 M, 50 mL) was used as the electrolyte.

A lead acid cell was equipped with carbon-based lead foam as its positive current collector and a lead slice as its negative current collector. The battery paste was prepared by a common method described in Ref. [13]. The amount of the positive active material applying on the carbon-based lead foam was 0.5 g, while the negative active material on the lead slice was 1.0 g. Subsequently, the electrodes were all cured at 80 °C for 48 h at a relative humidity of 90 % and dried at 80 °C for 12 h. The charge–discharge capacity was limited by positive electrode. Forming was performed in a 1.75 M H₂SO₄ solution with a charge of 600 Ah kg^{−1}PAM. Galvanostatic charge–discharge tests were performed on the cell using a Newware battery test system. The cell was charged to its 200 % initial discharge capacity at C/10 and then discharged at the same rate with the cut-off voltage of 1.7 V. A H₂SO₄ solution (4.5 M, 50 mL) was used as electrolyte for the charge–discharge cycles.

3 Results and discussion

3.1 Morphology of carbon-based lead foam

If carbon-based lead foam is served as positive current collector of lead acid battery, it not only has the similar chemical nature to that of lead plates, but also provides a large specific surface area and light quality, and thus can improve the battery's specific capacity. To achieve this goal, the lead coating must be dense and with a certain thickness. Dense lead coating can prevent the electrolyte from penetrating into the carbon foam substrate and prohibit the evolution of oxygen, so that the battery can be successfully charged. A certain thickness of the lead coating enables the carbon-based lead foam more resistant to corrosion, and to improve the life of the current collector.

Figure 1 is the SEM images of the carbon-based lead foam electrodeposited for 4 h in complex system. It can be seen from Fig. 1a that the lead coating can only cover the outside surface of carbon foam. The deep interior has even no lead on it. This is due to the low diffusion ability and low deposition rate of lead ions in complex system. Figure 1b

Table 1 Composition of the different lead electroplating bath and technical conditions

Complex system		Fluoborate system	
Pb(Ac) ₂ ·3H ₂ O	75 g L ^{−1}	Pb(BF ₄) ₂	250 g L ^{−1}
EDTA-Na ₂ ·2H ₂ O	100 g L ^{−1}	HBf ₄ (dissociative)	130 g L ^{−1}
NaAc	50 g L ^{−1}	Glutin	4 g L ^{−1}
Current density	0.2 A dm ^{−2}	Current density	0.2 A dm ^{−2}
Temperature	25 °C	Temperature	25 °C
Time	4 h	Time	4 h
pH	5~6	pH	<1

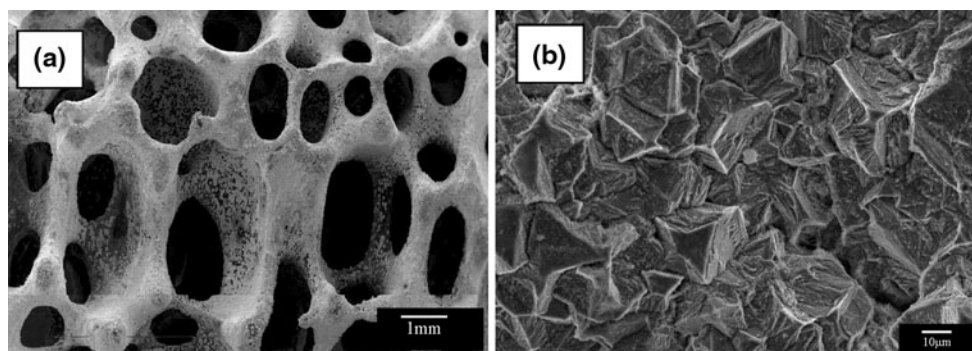


Fig. 1 SEM images of the carbon-based lead foam electrodeposited for 4 h from complex system **a** $\times 10$, **b** $\times 500$

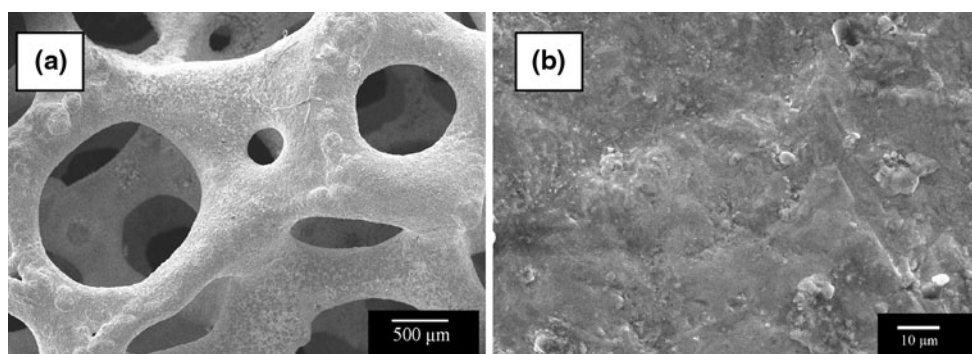


Fig. 2 SEM images of the carbon-based lead foam electrodeposited for 4 h from fluoroborate system **a** $\times 30$; **b** $\times 1,000$

shows that the lead coating in larger magnification is the aggregation of a number of loose particles, among which there are a lot of gaps. Thus this carbon-based lead foam obtained in the complex system cannot prevent electrolyte from contacting with the carbon substrate when it served as positive current collector for lead acid battery.

Figure 2 is the SEM images of the carbon-based lead foam electrodeposited for 4 h from fluoroborate system. The obtained lead coating shows a homogeneous dense coating covering over the whole carbon foam substrate, even on the internal surface in Fig. 2a. This means that the fluoroborate bath has a stable and good nature, which is suitable for electrodeposition on the complex-shaped substrate such as the carbon foam. Figure 2b shows in larger magnification that the lead coating formed in the fluoroborate system creates dense smooth surface. So, when the carbon-based lead foam obtained from fluoroborate system served as positive current collector, it could prevent the evolution of oxygen on the carbon substrate.

3.2 Electrochemical properties of carbon-based lead foam

As a lead acid battery current collector, carbon-based lead foam has to be stable in sulfuric acid. Cyclic voltammetry

(CV) was adopted to investigate the electrochemical properties of the carbon-based lead foam obtained from complex system and fluoroborate system, respectively. The carbon substrate and pure lead were also investigated comparatively. Figure 3 is the cyclic voltammograms of pure lead, carbon foam substrate and carbon-based lead foam from different systems. The curve (4) in Fig. 3 shows that the current of carbon substrate is great. This is because the surface area of carbon foam is very large and the oxygen evolution is severe in the positive potential range. The inherent nature of the carbon foam makes it not suitable for a lead acid battery positive current collector. The CV curve (1) of the pure lead shows a typical redox reaction of lead. The oxygen evolution potential on pure lead is up to 1.6 V, which is much lower than the electrochemical reaction potential of the positive active material in lead acid battery. Carbon-based lead foam from fluoroborate system has the similar CV curve to pure lead, indicating that they have similar electrochemical behavior in sulfuric acid. The lead coating is therefore proved to cover the whole carbon substrate completely. The CV curve of the carbon-based lead foam from complex system shows the carbon foam curve overlaying the pure lead one. Its current is large and the curve almost has no redox characteristic peaks of lead. This means that most of its

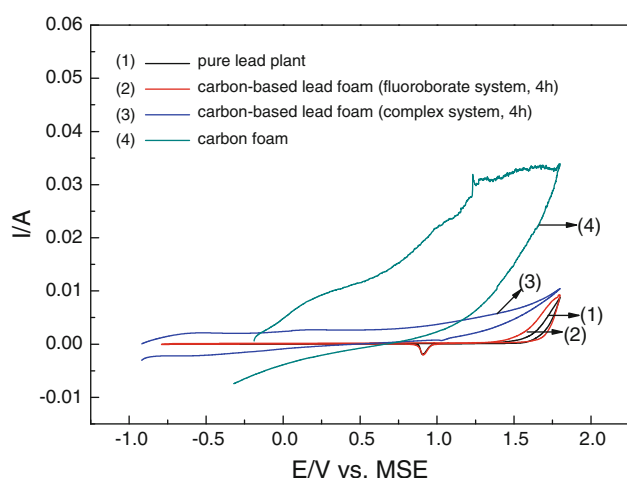


Fig. 3 Cyclic voltammograms of 1 pure lead; 2 carbon-based lead foam from fluoroborate system; 3 carbon-based lead foam from complex system; 4 carbon foam; Electrolyte: 4.5 M H_2SO_4 . Scan rate: 5 mV s^{-1}

surface was not covered by lead. This analysis is consistent with the previous SEM analysis.

3.3 Charge–discharge characteristics of lead acid battery with carbon-based lead foam

Carbon-based lead foam from fluoroborate system and complex system were used as positive current collector to assemble lead acid battery, respectively. Fig. 4 is the initial charge–discharge curve of lead acid battery with carbon-based lead foam from complex system. From the figure, it can be known that the battery can not be effectively charged and the discharge capacity is less than 12 % of the charged electricity. The battery totally cannot cycle. Figure 5 is the cycling property of lead acid battery with carbon-based lead

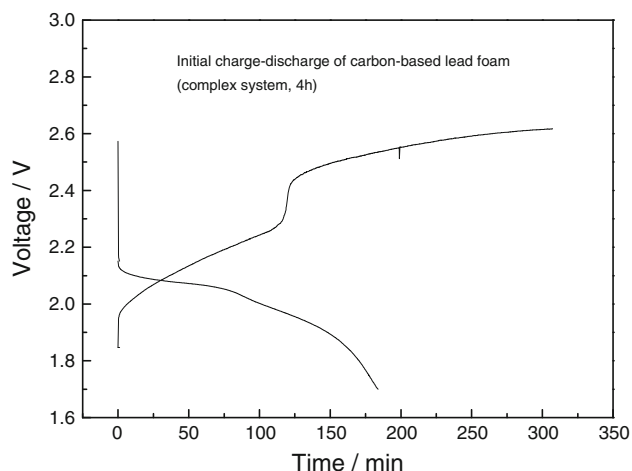


Fig. 4 Initial charge–discharge curves of lead acid battery with carbon-based lead foam from complex system

foam from fluoroborate system. Although the cycling performance of the battery with carbon-based lead foam (electrodeposition time 4 h) is not very stable, its maximum current efficiency is 65.7 % and the positive active material utilization rate is 59 %. The positive active material utilization of traditional lead acid battery was about 48–52 %. The carbon-based lead foam can serve as positive current collector for lead acid battery, and is superior to the traditional lead grid from this perspective. Carbon-based lead foam has a three-dimensional network structure, making the embedded active material has full access to the electric field of the collector and reacts completely. On the other hand, carbon-based lead foam can support the active material and prevent the active material from falling off the electrode. These are favorable for improving the cycle life of the lead acid battery. The discharge performance of lead acid battery with carbon-based lead foam (electrodeposition time 2 h) are not satisfying. When the lead acid battery cycled 20 times, it can not discharge any more and its maximum current efficiency is only 25.4 %. This phenomenon may be due to the unqualified lead coating.

3.4 Failure analysis of carbon-based lead foam

The failure of the traditional grid of lead acid batteries is usually due to the active material breaking off or irreversible sulfation on negative electrode. The failure of the lead acid battery with carbon-based lead foam does not rule out the above two reasons. To better understand the failure mechanisms of the lead acid battery with carbon-based lead foam, the carbon-based lead foam (electrodeposition time 4 h and 2 h) after 20 charge–discharge cycles was studied by scanning electron microscope. The images are shown in Fig. 6a, b, respectively. Fig. 6a shows compact structure and good contact between carbon substrate surface, lead

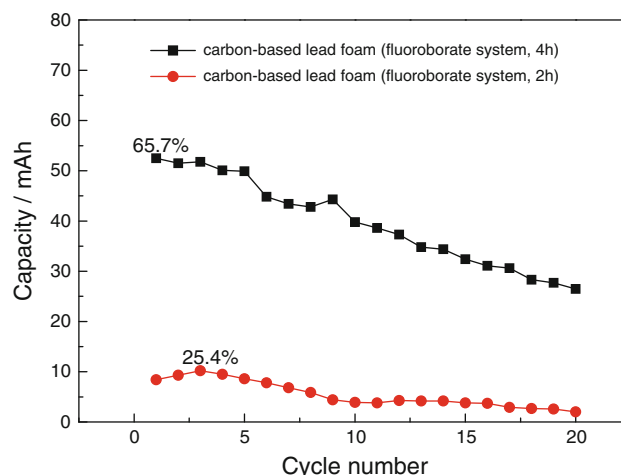


Fig. 5 Cycling property of lead acid battery with carbon-based lead foam from fluoroborate system

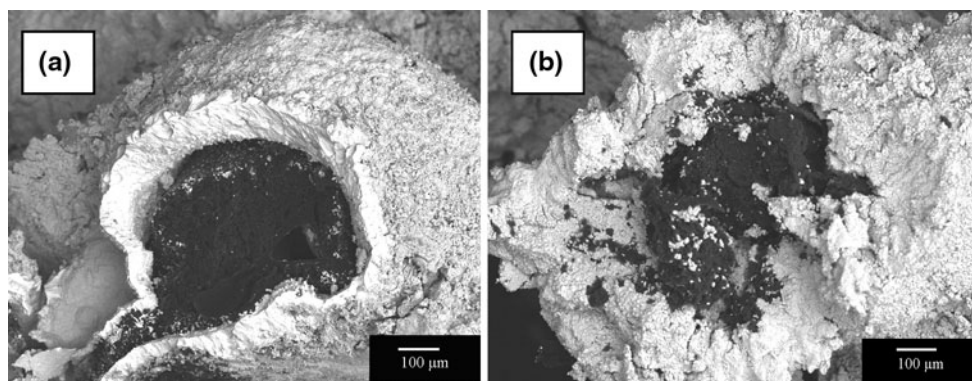


Fig. 6 SEM images of carbon-based lead foam after 20 charge–discharge cycles **a** unfailed; **b** failed

coating and active material. So, the unstable cycling performance (shown in Fig. 5) of the battery with carbon-based lead foam (electrodeposition time 4 h) is not because the lead coating unstable or easy to damage. The reason for significant fading of the capacity in Fig. 5 is mainly attributed to the inadequate activation of the active materials during cycles, which can be improved by controlling the charging and discharging conditions. Fig. 6b shows that the failed carbon-based lead foam collapsed. There were many cracks on the active material layer and lead coating layer. And the carbon substrate becomes loose. The reason for the failure of lead acid battery is probably because the lead coating is not dense and thick enough, resulting in corrosion and electrolyte penetration into the carbon foam substrate to damage the structure of the positive electrode at last.

Figure 7 shows the surface morphology of carbon-based lead foam electrodeposited in fluoroborate system for 2 h. It is seen that the surface exhibits parts of smooth lead coating and parts of porous morphology. So it can be speculated that at the initial stage the lead deposited on the irregular uneven carbon foam at different nucleation and growth rates, resulting in deposition areas separated from each other. With the deposition continuing, the deposition area expands and gradually merges into a dense homogeneous whole. The carbon foam substrate was then coated completely finally. So it is known that not only the suitable plating electrolyte system, but also the deposition time is crucial for a qualified lead coating of carbon-based lead foam.

Figure 8 shows the cyclic voltammograms of carbon-based lead foam electrodeposited for 4 and 2 h, respectively. It is found that carbon-based lead foam electrodeposited for 2 h shows the electrochemical properties of the corresponding redox peaks of pure lead. However, the large overall current also shows the carbon foam substrate features. This means that the carbon-based lead foam from fluoroborate system for 2 h gets better coverage than the one obtained from the complex system for 4 h (see Fig. 3), but

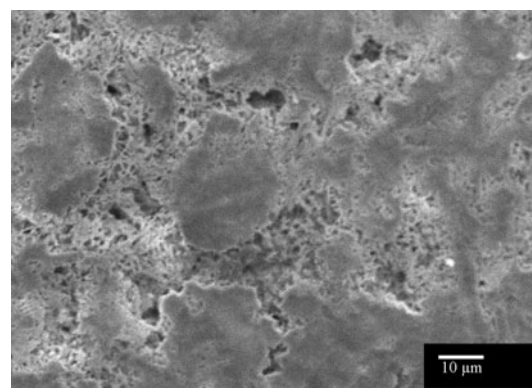


Fig. 7 SEM images of carbon-based lead foam electrodeposited from fluoroborate for 2 h

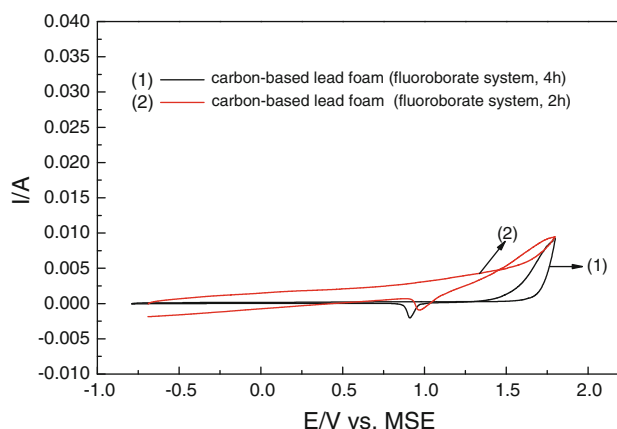


Fig. 8 Cyclic voltammograms of carbon-based lead foam electrodeposited for 4 and 2 h

still not thick and dense enough, and cannot completely prevent the electrolyte get into the foam substrate. So, the unqualified density and thickness of the lead coating are the main reasons for the failure of the battery with carbon-based lead foam.

4 Conclusion

- (1) The carbon-based lead foam with a certain thickness of uniform dense lead coating was successfully prepared from fluoroborate plating systems under proper conditions. The electrochemical property of the carbon-based lead foam is similar to that of metallic lead.
- (2) The lead acid battery with carbon-based lead foam as positive current collector shows high discharge capacity and high cycle stability, which means that the carbon-based lead foam can be used as lead acid battery's positive electrode current collector.
- (3) The failure mechanism of the carbon-based lead foam demonstrated that the quality and thickness of lead coating are key factors to improve the performance of the lead acid battery with carbon-based lead foam.

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